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(54) Title: COATED STRUCTURAL ARTICLES (57) Abstract A structural article comprises a substrate having an ionic charge which is coated with a coating having essentially the same ionic charge. The coating consists essentially of a filler material and a binder material. The substrate is preferably fiberglass, the filler is preferably fly ash and the binder material is preferably acrylic latex. The substrate is preferably bonded together using a mixture of urea formaldehyde and standard acrylic. In a preferred embodiment, the coating comprises nearly 85 % of the structural article and fly ash comprises approximately 85 % to 95 % of the coating.		

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COATED STRUCTURAL ARTICLES

SPECIFICATION

BACKGROUND OF THE INVENTION

This invention relates to structural articles and a method for making
5 such articles comprising a substrate having an ionic charge coated with a coating
having essentially the same charge and consisting essentially of a filler material and a
binder material.

For many years substrates such as fiberglass have been coated with
various compositions to produce structural articles having utility in, among other
10 applications, the building industry. U.S. Patent No. 5,001,005 relates to structural
laminates made with facing sheets. The laminates described in that patent include
thermosetting plastic foam and have planar facing sheets comprising 60% to 90% by
weight glass fibers (exclusive of glass micro-fibers), 10% to 40% by weight non-glass
filler material and 1% to 30% by weight non-asphaltic binder material. The filler
15 materials are indicated as being clay, mica, talc, limestone (calcium carbonate),
gypsum (calcium sulfate), aluminum trihydrate (ATH), antimony oxide, cellulose
fibers, plastic polymer fibers or a combination of any two or more of those
substances. The patent further notes that the filler materials are bonded to the glass
fibers using binders such as urea-, phenol- or melamine-formaldehyde resins (UF, PF,
20 and MF resins), or a modified acrylic or polyester resin. Ordinary polymer latexes
used according to the disclosure are Styrene-Butadiene-Rubber (SBR), Ethylene-
Vinyl-Chloride (EVC), PolyVinylidene Chloride (PvdC), modified PolyVinyl
Chloride (PVC), PolyVinyl Alcohol (PVOH), and PolyVinyl Acetate (PVA).

U.S. Patent No. 4,745,032 discloses an acrylic coating comprised of
25 one acrylic underlying resin which includes fly ash and an overlying acrylic resin
which differs from the underlying resin.

U.S. Patent No. 4,229,329 discloses a fire retardant coating composition comprising fly ash and vinyl acrylic polymer emulsion. The fly ash is 24 to 50% of the composition.

Many different coating compositions have been formulated over the
5 years but often such compositions would bleed through substrates, such as fiberglass substrates, if the substrates were coated on just one side unless the compositions had a high binder content and/or included viscosity modifiers to enhance the viscosity of the coating composition. To prevent bleed through, such coating compositions sometimes had their viscosity increased by blowing or whipping air into the
10 compositions. Although such blown compositions did not bleed through to the other side of mats such as fiberglass mats, the raw material costs for the compositions were high because of the numbers of constituent elements involved.

Accordingly, it is an object of this invention to provide a structural article having a coating which includes only two major constituents, while eliminating
15 the need for viscosity modifiers, for stabilizers or for blowing. It is also an object of this invention to provide a low cost, relatively light weight structural article comprised principally of a coating having a low binder content and a high filler content. It is a further object of this invention to provide a relatively light weight, low cost coating which coats a substrate without bleeding through the substrate.

20

SUMMARY OF THE INVENTION

In accordance with the invention, a structural article is made by coating a substrate having an ionic charge with a coating having essentially the same ionic charge. The coating consists essentially of a filler material and a binder material. By coating the substrate with a coating having essentially the same ionic charge, the
25 applicant has developed a zero bleed through product while using only two major ingredients in the coating and eliminating the need for costly and time consuming processing steps such as blowing. Applicant has discovered that by producing a coating having essentially the same ionic charge as the substrate, a zero bleed through product may be produced having a low binder content and no viscosity modifiers.

The coated substrate of the present invention may be any suitable reinforcement material capable of withstanding processing temperatures, such as glass fibers, polyester fibers, cellulosic fibers, asbestos, steel fibers, alumina fibers, ceramic fibers, nylon fibers, graphite fibers, wool fibers, boron fibers, carbon fibers, jute
5 fibers, polyolefin fibers, polystyrene fibers, acrylic fibers, phenolformaldehyde resin fibers, aromatic and aliphatic polyamide fibers, polyacrylamide fibers, polyacrylimide fibers or mixtures thereof which may include bicomponent fibers.

Preferably, the filler is class F fly ash and 90% to 95% by weight of the fly ash is aluminosilicate. Such a fly ash, known as Alsil O4TR, is produced by
10 JTM Industries of Kennesaw, Georgia.

The coating is prepared by using a binder material such as a high performance heat-reactive acrylic latex polymer to bond the filler materials together and to bond the filler to the substrate. Such a binder material is Hycar 2679 acrylic latex polymer supplied by B.F. Goodrich Company of Cleveland, Ohio. It is
15 believed, however, that any linear polymer, linear copolymer or branched polymer may be useful in preparing the coating. Possible binder materials include butyl rubber latex, SBR latex, neoprene latex, polyvinyl alcohol emulsion, SBS latex, water based polyurethane emulsions and elastomers, vinyl chloride copolymers, nitrile rubbers and polyvinyl acetate copolymers.

20 In a preferred embodiment, the coating comprises nearly 85% by weight of the structural article. In that coating, approximately from 84% to 96% by weight is fly ash and the remainder is the acrylic latex binder. The substrate comprises about 15% by weight of the structural article. Glass fibers comprise approximately 12% by weight of the article and a binder material comprises about 3%
25 by weight of the article. The binder which bonds together the glass fibers is from 99% to 75% (preferably 98% to 94%) by weight urea formaldehyde and from 1% to 25% (preferably 2% to 6%) by weight standard acrylic latex.

The substrate may be coated by air spraying, dip coating, roll coating or film application such as lamination/heat pressing. The coating may be bonded to
30 the substrate by chemical bonding, mechanical bonding and/or thermal bonding.

Mechanical bonding is achieved by force feeding the coating onto the substrate with a knife.

Structural articles made in accordance with this invention may be of any shape and may be used in any of a variety of products including roofing shingles, structural laminate facing sheets, building air duct liners, roofing underlayment (or
5 roofing felt), underlayment for organic shingles to provide Class "A" U.L. rating, built up roofing materials, roll roofing, modified roll products, filter media (including automotive filters), automotive hood liners, head liners, fire walls, vapor barriers etc. Preferably, such articles are planar in shape. The substrate is coated on one side or
10 both sides depending on the intended application. For instance, if one side of the substrate is coated with the filler/binder coating, the other surface can be coated with conventional roofing asphalt, modified asphalts and non-asphaltic coatings, and the article can then be topped with roofing granules. It is believed that such roofing material could be lighter in weight, offer better fire resistance and better performance
15 characteristics (such as cold weather flexibility, dimensional stability and strength) than prior art roofing materials.

Additionally, the structural article may be coated with a water repellent material. Two such water repellent materials are Aurapel 33R and Aurapel 391 available from the Auralux Corporation of Norwich, Connecticut. It is believed that
20 wax emulsions, oil emulsions, silicone emulsions, polyolefin emulsions and surfonys as well as other similar performing products may also be suitable water repellent materials. Further, structural articles made in accordance with the invention may be coated with an algacide such as zinc powder, copper oxide powder or the herbicides Atrazine available from e.g. Ribelin Industries or Diuron available from e.g. Olin
25 Corporation, an antifungal material such as Micro-Chek 11P, an antibacterial material such as Micro-Chek 11-S-160, a surface friction agent such as Byk-375, a flame retardant material such as ATH (aluminum trihydrate) available from e.g. Akzo Chemicals and antimony oxide available from e.g. Laurel Industries and/or a coloring dye such as T-1133A and iron oxide red pigments, and other products which can
30 impart specific surface functions. The Micro-Chek products are available from the

Ferro Corporation of Walton Hills, OH. Byk-375 may be obtained from Wacker Silicone Corporation of Adrian, MI and T-1133A is sold by Abco Enterprises Inc. of Allegan, MI. The additional coatings of, e.g. water repellent material, antifungal material, antibacterial material, etc., may be applied to one or both sides of structural articles otherwise having filler/binder coatings on one or both sides of a substrate. For example, structural articles comprising substrates coated on one or both sides with filler/binder coatings could be coated on one side with a water repellent composition and on the other side with an antibacterial agent..

Applicant's invention also involves a method for making a structural article comprising the steps of coating a substrate having an ionic charge with a coating having essentially the same ionic charge. The coating consists essentially of a filler material and a binder material. In one embodiment, the coating is prepared by mixing the filler material and the binder material until the ionic charge of the mixed materials changes such as to increase the viscosity of the coating. In the preferred embodiment, the substrate is anionic and the coating is essentially anionic even though the cationic nature of the coating increases during the aforementioned mixing.

DETAILED DESCRIPTION

Structural articles are made by coating a substrate having an anionic charge with a coating having essentially the same ionic charge. Any suitable reinforcement material capable of withstanding processing temperatures may be employed as a substrate in accordance with the invention. Examples include, inter alia, glass, fiberglass, ceramics, graphite (carbon), PBI (polybenzimidazole), PTFE, polyaramides, such as KEVLAR and NOMEX, metals including metal wire or mesh, polyolefins such as TYVEK, polyesters such as DACRON or REEMAY, polyamides, polyimides, thermoplastics such as KYNAR and TEFZEL, polyether sulfones, polyether imide, polyether ketones, novoloid phenolic fibers such as KYNOL, cotton, asbestos and other natural as well as synthetic fibers. The substrate may comprise a yarn, filament, monofilament or other fibrous material either as such or assembled as a textile, or any woven, non-woven, knitted, matted, felted, etc. material. The

polyolefin may be polyvinyl alcohol, polypropylene, polyethylene, polyvinyl chloride, polyurethane, etc. alone or in combination with one another. The acrylics may be DYNEL, ACRILAN and/or ORLON. RHOPLEX AC-22 and RHOPLEX AC-507 are acrylic resins sold by Rohm and Haas which may also be used. The
5 cellulosic fibers may be natural cellulose such as wood pulp, newsprint, Kraft pulp and cotton and/or chemically processed cellulose such as rayon and/or lyocell.

The fly ash referred to in the examples was obtained from JTM Industries, Inc. of Martin Lake and Jewett, Texas and had a particle size such that less than 0.03 % remained on an agitated 0.1 inch X 0.1 inch screen. Black colorant or
10 pigment used in various of the articles of the examples was T-113A sold by Abco, Inc.

Foamed structural articles made in accordance with the present invention may be made by any of the known methods for making foamed compositions such as, for example, aeration by mechanical mixing and the other
15 techniques described in U.S. Patent No. 5,110,839.

EXAMPLE I

To reduce the weight and cost of coated structural articles, the applicant formulated the coating using only three ingredients: water, BF Goodrich acrylic latex Hycar 2679 and JTM Alsil O4TR fly ash filler. The amounts of the three
20 constituents were as follows: 19% water, 6% Hycar 2679, 74% JTM fly ash. Dye and defoaming agent made up 1% of the formulation. Generally, the coating should be produced by combining 50% to 80% fly ash filler, 1% to 25% acrylic latex binder, 15% to 25% water and minor amounts of dye and defoaming agent as needed. The defoaming agent was Drew Plus Y-250 sold by Drews Industrial Division of Boonton,
25 NJ. The materials were mixed in a reaction or mixing kettle for 45 minutes. JTM fly ash filler comprised a much higher percentage of the coating than the 40-45% by weight filler which is the industry standard. Moreover, the binder content was lower than amounts usually found in such coating formulations.

The coating was used to coat a fiberglass mat on one side. The mat

was manufactured by Elk Corporation of Ennis, Texas and had a basis weight in the range of 1.4 lb./sq. to 2.0 lb./sq. The mat had a porosity in the range of 800 to 1,000 cfm. Heretofore, when such highly porous mats have been coated on one side only, it was expected that the coating would bleed through to the other side. In accordance with the present invention however, the novel coating coated the surface of the fiberglass mat very well and did not bleed through to the other side of the mat. The coated article was durable and flexible and did not crack on bending. Typical tensile strength measurements were as follows: machine direction 156 lbs.; cross direction 57 lbs.; average 107 lbs. Typical tear strength measurements were as follows: machine direction 151 grams; cross direction 306 grams; average 229 grams.

The coated article was hand brushed with adhesive to determine if there was bleed through to the other side of the article. No bleed through was observed. Further, the coated article was soaked in unleaded gasoline for 48 hours and no change in the physical state of the article was observed. There was no degradation and no reaction. The coated article was also checked for combustibility. When exposed to flame it burned, but when the flame was removed the burning stopped.

Surprisingly, when the coating of the present invention was used to coat the fiberglass mat on one side, it did not bleed through to the other side even though the coating had a relatively low viscosity of 700 cp. Although not wishing to be bound by any particular theory, the applicant believes that the coating did not bleed through the mat because the fiberglass mat is anionic and the coating of the present invention (when wet) includes a combination of water and Hycar 2679 (which together are anionic) and JTM filler (which is also anionic). The addition of the JTM filler to the acrylic latex in water results in a repulsion of charges and low viscosity. Although low viscosity is not a desired objective for coating a highly porous mat, the unique characteristic of the invention is that the coating does not bleed through regardless of the viscosity because the mat is also anionic and like charges repel each other just as the north pole of one magnet repels the north pole of another magnetic.

If desired, however, the viscosity of the coating can be increased

through mixing. It is believed that JTM Alsil-O4TR fly ash filler is approximately 90% to 95% aluminosilicate, which is unaffected by water, but in acidic solution undergoes hydrolysis. The water and latex solution to which JTM fly ash filler was added is acidic in nature and, on prolonged mixing, there is some hydrolyzation of the aluminosilicate thereby increasing the viscosity of the coating. The longer or the more rapidly the coating is mixed, the higher the viscosity. However, the coating still maintains an essentially anionic charge and thus there is still repelling of charges between the coating and the substrate.

Whether slowly or rapidly mixed, the coatings of the present invention may be applied to the substrates in relatively uniform thin coats because the like charges among the filler and acrylic latex elements in the coating repel one another. Thus, it is believed that the ionic charge repulsion characteristic which prevents the coating from bleeding through the mat also enables the application on the mat of a relatively uniform thin film coating. In instances where, due to price, supply or other considerations, the filler material to be employed has an ionic charge which is essentially the opposite of the charge of the substrate, modifiers are available to coat the filler material so that ultimately the coating and substrate of the article have essentially the same ionic charge. It is believed that viscosity modifiers could serve such a purpose.

20

EXAMPLE II

Water, Hycar 2679 acrylic latex and JTM Alsil-O4TR fly ash were combined in the same amounts as noted in Example I. However, in accordance with another embodiment of the invention, the materials were mixed for a longer period, 7 hours, in the same reaction/mixing vessel with a paddle mixer. The coating had a viscosity of about 40,000 cp. The coating was then applied to the same type of mat using the same technique as recited in Example I. The tensile and tear strengths of the coated article were the same as in Example I. The viscosity of the materials increased during mixing in both Examples I and II. However, relatively rapid mixing such as in Example I results in the production of foam which was observed in only small

amounts in Example II which was mixed more slowly. Accordingly, a defoaming agent is added when the materials are mixed rapidly.

The invention provides a coated fabric which is rigid in nature and is also flexible enough to be rolled up, showing no signs of cracking, etc. The coated fabric has a porosity of less than 1.0 cfm and adheres very well to polyurethane foam, isocyanurate foam, asphaltic compounds, and granules (non-asphaltic shingle components).

The coated product may have few pinholes or may have numerous pinholes and still maintain a porosity of less than 1.0 cfm when coated with solvent based adhesive such as Firestone Bonding Adhesive BA-2004, i.e. the adhesive did not bleed to other side.

The coated articles were made water repellent by coating with further additives, Aurapel 33R and Aurapel 391, which can be obtained from Auralux Corporation. The coating was accomplished by diluting the coating compound with water and then kiss coating the articles on one side while they were being coated on the other side by standard coating techniques which included the use of a doctor blade.

Prior to coating with a water repellent coating, the novel coating of the present invention can be treated with pigment or dye or any other suitable coloring means to give color to the structural articles of the invention. For instance, a carbon black pigment (0.5% by weight) was added to the coating composition of the Examples to give color texture to the finished coating on the fiberglass mat.

Besides water repellent treatment, the structural articles of the present invention can be coated with antifungal, antibacterial and surface friction agents, an algacide and/or a flame retardant material by mixing with the coating constituents prior to coating the substrate or by spraying on the partly finished articles at some point in the processing, e.g. between drying and curing.

Coating of the fiberglass substrates was accomplished by the applicant using a hand-held coater which can be obtained from the Gardner Company, but any conventional method, such as spraying, dipping and flow coating from aqueous or

solvent dispersion, calendering, laminating and the like, followed by drying and baking, may be employed to coat the substrate as is well known in the art. Additionally, the coating may be separately formed as a film of one or more layers for subsequent combination with the substrate.

- 5 It should be understood that the above examples are illustrative, and that compositions other than those described above can be used while utilizing the principals underlying the present invention. For example, other sources of filler as well as mixtures of acrylic latex and/or surfactants can be used in formulating the structural articles. Moreover, the coating compositions can be applied to various
- 10 types of substrates, as described above.

CLAIMS

1. A structural article comprising a substrate having an ionic charge coated with a coating having essentially the same ionic charge wherein said coating consists essentially of a filler material and a binder material and wherein said binder material bonds the filler material together and to the substrate.
5
2. A structural article according to claim 1 wherein said substrate is fiberglass, said filler is fly ash and said binder is acrylic latex.
3. A structural article according to claim 2 wherein said substrate is planar and is coated on one side with said coating.
- 10 4. A structural article according to claim 2 wherein said substrate is planar and is coated on both sides with said coating.
5. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with a water repellent material.
- 15 6. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with an antifungal material.
7. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with an antibacterial material.
8. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with a surface friction agent.
- 20 9. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with a flame retardant material.

10. A structural article according to claims 1, 3 or 4 wherein said article is coated on one or both sides with an algacide.

11. A structural article according to claims 1, 3 or 4 wherein said article is colored with dye on one or both sides.

5 12. A structural article according to claims 2, 3 or 4 wherein said substrate is bonded together by a binder material consisting essentially of urea formaldehyde and acrylic latex.

13. A structural article according to claims 2, 3 or 4 wherein
a) said article is from 10% to 25% by weight glass fibers;
10 b) said glass fibers are bonded together by a mixture of from 99% to 75% urea formaldehyde and from 1% to 25% acrylic latex;
c) said coating is from 84% to 96% fly ash filler and, from to 16% to 4% acrylic latex binder material.

14. A method for making a structural article comprising the steps of
15 coating a substrate having an ionic charge with a coating having essentially the same ionic charge wherein said coating consists essentially of a filler material and a binder material and wherein said binder material bonds the filler material together and to the substrate.

15. A method according to claim 14 wherein
20 a) said coating is prepared by mixing the filler material and the binder material until the viscosity of the coating increases; and
b) the substrate is then coated with the more viscous coating.

INTERNATIONAL SEARCH REPORT

Inter. .nal Application No

PCT/US 98/12959

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C B32B C08K E04D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 229 329 A (H. BENNETT) 21 October 1980 cited in the application see column 1, line 48 - column 2, line 30 ---	1-15
X	US 5 001 005 A (R.H. BLANPIED) 19 March 1991 cited in the application see column 2, line 62 - column 3, line 21 ---	1-15
A	DATABASE WPI Section Ch, Week 8923 Derwent Publications Ltd., London, GB; Class A93, AN 89-171160 XP002079625 & RO 96 083 A (TRUST ANTR GEN CONS) , 10 November 1988 see abstract --- -/--	1-15

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☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 232 530 A (A.B. MALMQUIST) 3 August 1993 see claim 5	1
A	WO 82 00269 A (D. FERZIGER ET AL) 4 February 1982 see claims 1-4	1-15

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. Application No

PCT/US 98/12959

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4229329 A	21-10-1980	NONE	
US 5001005 A	19-03-1991	US 5112678 A US 5102728 A	12-05-1992 07-04-1992
US 5232530 A	03-08-1993	US 5305569 A	26-04-1994
WO 8200269 A	04-02-1982	US 4526830 A AU 551360 B AU 7451781 A BE 889724 A BR 8108710 A CA 1208987 A DK 77282 A EP 0056405 A FI 820693 A,B, IE 52133 B IN 163193 A IN 155841 A JP 57501240 T US 4801493 A	02-07-1985 24-04-1986 16-02-1982 16-11-1981 22-06-1982 05-08-1986 23-02-1982 28-07-1982 26-02-1982 08-07-1987 20-08-1988 16-03-1985 15-07-1982 31-01-1989

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